Data Evaluation Report of Hydrolysis in Soil/Water Systems

PMRA Submission Number {.....} EPA MRID Number 42937006

Data Requirement: PMRA Data Code: N/A
EPA DP Barcode: 330489
OECD Data Point: N/A
EPA Guideline: N/A

Test material:
Common name:
Chemical name
IUPAC: (*R*)-2-(2,4-dichlorophenoxy)propionic acid
CAS name: (2*R*)-2-(2,4-dichlorophenoxy)propanoic acid
CAS No:
Synonyms: 2,4-DP-p
PC Code: 031465

Primary Reviewer: James Hetrick, Ph.D.
EPA
Signature: James Hetrick
Date: 10-29-10

Secondary Reviewer: Robert Miller
EPA
Signature: Robert A. Miller
Date: 10.04.10

Company Code:
Active Code:
Use Site Category:

CITATION:

Skinner, Wayne. 1993. Hydrolysis of Optically Active [^{14}Cl]- 2- (2,4-Dichlorophenoxy) propionic Acid 2-Ethylhexyl Ester in Soil/Water Systems. Performed by PTRL West, Inc., Richmond, CA. Submitted by 2,4-DP(1988) Task Force, BASF, Germany. MRID 42937006

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EXECUTIVE SUMMARY:

The study provides supplemental data on the degradation of 2,4-DP-p-2-ethylhexyl ester (2,4-DP-EHE) in soil slurries. Radiolabeled 2,4-DP-EHE had a half-life of 12 hours in slurries of acidic silty clay loam soil and 24 hours in slightly-acidic sandy loam soil. Radiolabeled degradates were identified as 2,4-DP-p acid and 4 chlorophenoxy-propionic acid (4-CPP). Unidentified radiolabeled degradates were detected in soil extracts. The reported data indicate that 2,4-DP-EHE should not persist in hydro-soils and sediment.

MATERIALS AND METHODS:

Surface soil samples from a Lowell silty clay and a Huntington silt loam were passed through a 2mm sieve and stored at a field moist condition in a sealed container. Physicochemical and microbiological properties of the test soils are shown in Tables II and III.

Preliminary Study

A subsample (7 g dry weight) of test soil was placed into each of four 50 ml glass centrifuge tubes. Each soil sample was suspended in sterile 0.01N $CaC1_2$ with a nominal [^{14}C]-2,4- DP-EHE concentration (radio purity = 95.6%; optical purity = 93.5%; SA = 1.59 MBq/mg. (Reviewer Note: the water solubility of 2,4-DP EHE is approximately 170 µg/ml). Each test tube was capped, vortexed, and incubated at 25°C for 30 minutes and 4 hours post-treatment.

Definitive Study

A subsample (7 g dry weight) of each test soil was placed into each of twelve 50 ml glass centrifuge tubes. Each soil sample was suspended in sterile 0.01N $CaC1_2$ with a nominal [^{14}Cl]-2,4-DP-EHE concentration (radio purity = 95.6%; optical purity = 93.5%; Specific Activity =1.59 MBq/mg. (**Reviewer Note**: The water solubility of 2,4-DP-EHE is approximately 170 µg/ml). The soil solution ratio was maintained at 5. Each test tube was capped, vortexed, and incubated at 25°C in the dark. Duplicate samples of the sandy loam soil were taken immediately post-treatment, 2, 4, 8, 12, and 24 hours post-treatment. Duplicate samples of the silty clay loam soil were taken immediately post-treatment, 4, 8, 12, 24, and 48 hours post-treatment.

Analytical

Each soil slurry was shaken and allowed to settle for 1 minute. The pH of the solution was determined by litmus paper. Each soil slurry was acidified (pH 2-4) with 6N HC1 and then centrifuged to separate soil and supernatant. The supernatant was decanted for chemical analysis. 4 hour samples were sequentially extracted with acetone and acetone: water 9:1 (v:v). The soil extracts were combined for chemical analysis. Soil extracts and supernatant samples were stored frozen (< 0°C) for 4 days and 24 hours, respectively, before chemical analysis.

Soluble residues were separated using 2D-TLC with toluene/ethyl acetate/acetic acid 10:1:1 (v:v:v) and hexane/2-propanol 1:1(v:v) with 5% acetic acid. Secondary confirmation of radiolabeled 2,4-DP-EHE, 2,4-DP-p, 4-CPP in the 48 hour soil extract of the sandy Loam soil was conducted by 2-D TLC. Soluble radiolabeled 4-CPP and 2,4-DP-p acid in the 4 hour water samples and the 48 hour soil extract of the sandy loam soil were separated by reverse phase HPLC using a solvent system of acetonitrile: HPLC water:1% trifluoroacetic acid system; separated residues in HPLC eluent were collected in fraction collector at 8.5 minute intervals. Separated residues were identified by co-chromatgraphy with known standards. The ^{14}C content in water samples and HPLC eluent were determined by LSC. The ^{14}C content of extracted soil was determined by combustion- LSC. The 2,4-DP-p EHE was purified using TLC separation. The optical purity of 2,4-DP-EHE was determined by HPLC equipped with a Nucleosil Chiral-2 column and isocratic solvent system of 0.1% isopropanol in hexane; separated residues were detected using a UV detector.

RESULTS AND DISCUSSION:

A. The material balance of radiolabeled residues ranged from 97.7 to 108% for applied 2,4-DP-p EHE in silt loam and sandy loam soil slurries (Tables IV and VII).

B. The half-life of 2,4-DP-EHE was 12 hours and 24 hours in a silty clay loam and sandy loam slurries, respectively (Tables VI and IX).

C. Degradates of 2,4-DP-EHE in soil/water slurries were 2,4-DP-p acid (maximum concentration 28% of applied at 4 hours post-treatment) and 4-CPP (maximum concentration 2% of applied at 24 hours post-treatment). Unidentified residues were detected in soil (2 % of applied) and water (<0.24% of applied). Four different peaks were eluted from soil extracts. Unidentified, non-extractable radiolabeled residues were also detected (2 to 3% of applied) in soil.

D. The degradation of 2,4-DP-p EHE in soil slurries is dependent on the cleavage of the ester bond to form 2,4-DP-p acid.

REVIEW COMMENTS:

A. EFED recognizes the soil slurry study was designed to assess the persistence of 2,4-DP-EHE in soil. EFED believes the study conditions are representative of a flooded soil or aquatic sediment. EFED notes that 2,4-DP- EHE degradation rate in soil may vary from soil slurry studies. However, the reported data indicate 2,4-DP-EHE should not persist in acidic sediment/hydro-soil.

B. The registrant did not analyze soil slurries for the expected degradate 2-ethylhexanol. EFED believes 2-ethylhexanol will be formed through the de-esterification of 2,4- DP-EHE.

Table II. Characteristics of the Silty Clay Loam and Sandy Loam Soils Used in tnis Study.

Source: PTRL East

Soil characteristics were conducted at: PTRL East, Inc.
Richmond, Kentucky 40475

Summary of Results

	Silty Clay Loam	Sandy Loam
pH	4.99	6.8
CEC (meq/100g)	16.1	5.5
Organic Carbon (%)	0.71	1.00
WHC (%) @ 1/3 Bar	28.3	15.1
Sand (%)	15	67
Silt (%)	54	23
Clay (%)	31	10
Soil Classification	Silty Clay Loam	Sandy Loam
Location	Madison County, KY	Fayette County, KY
Series	Lowell Silty Clay	(From Huntington Silt Loam Series)

Table III. Microbiological Profiles of Silty Clay Loam and Sandy Loam Soils Used in this Study.

	Soil Type	
	Silty Clay Loam (CFU/g)[a]	Sandy Loam (CFU/g)[a]
Total Aerobic Bacteria	3.15×10^6	10.0×10^6
Total Actinomycetes	2.2×10^6	6.1×10^6
Total Fungi	0.047×10^6	0.058×10^6

a Colony Forming Units per gram.

Table IV. Accountability and Extractability of Radiocarbon from Soil Slurry Hydrolysis of 2,4-DP-p 2-EHE in Silty Clay Loam Soil Following Application at 3.0 ppm.

Sample	DPM Applied	Water Phase			Total DPM Combined Soil Extracts[a]	Total DPM Soil Residual Solids	Total DPM Recovered	Percent Recovery[b]
		DPM/mL	mL in Supernatant	Total DPM in Supernatant				
0 Hr A	1,998,917	2,880	31.0	89,280		1,881,638	1,970,918	98.6
0 Hr B	1,998,917	2,694	31.5	84,861		1,916,502	2,001,363	100.1
2 Hr A	1,998,917	12,395	31.0	384,245		1,586,612	1,970,857	98.6
2 Hr B	1,998,917	12,173	31.0	377,363		1,665,135	2,042,498	102.2
4 Hr A	1,998,917	16,948	31.5	533,862		1,503,162	2,037,024	101.9
4 Hr B	1,998,917	18,193	31.5	573,080		1,471,220	2,044,300	102.3
8 Hr A	1,998,917	28,502	31.5	897,813		1,121,244	2,019,057	101.0
8 Hr B	1,998,917	27,157	31.5	855,446		1,097,568	1,953,014	97.7
12 Hr A	1,998,917	38,228	31.0	1,185,068		864,737	2,049,805	102.5
12 Hr B	1,998,917	33,467	31.5	1,054,211		939,913	1,994,124	99.8
24 Hr A	1,998,917	41,597	31.5	1,310,306	694,361	39,128	2,043,795	102.2
24 Hr B	1,998,917	40,581	31.5	1,278,302	725,010	41,603	2,044,915	102.3

a Only the 24 hour soil pellets were extracted.

b The percent recovery of applied radiocarbon had an overall mean ± S.D. of 100.8 ± 1.7 % for all samples.

Table VI. **Distribution of Radiocarbon in the Water Phase and Soil Pellet Extracts from Soil Slurry Hydrolysis of 2,4-DP-p 2-EHE in Silty Clay Loam Soil.**

	PERCENT OF APPLIED DOSE															
Sample	Total in Water Phase[a]	Product Distribution in Water Phase				Total in Soil Extract	Product Distribution in Soil Extract				Product Distribution in Total System					
		2,4-DP-p: Ester	2,4-DP-p: Acid	4-CPP Acid[b]	Un-knowns		2,4-DP-p: Ester	2,4-DP-p: Acid	4-CPP Acid[b]	Un-knowns	2,4-DP-p: Ester	2,4-DP-p: Acid	4-CPP Acid[b]	Un-knowns	Unextractable	Total
0 Hr Rep A	5.0	n.d.	n.d.	n.d.	n.d.	n.d.										
0 Hr Rep B	4.7	n.d.	n.d.	n.d.	n.d.	n.d.										
average	4.9															
2 Hr Rep A	21.7	1.6	18.7	1.3	0.04	n.d.										
2 Hr Rep B	21.3	1.1	18.7	1.2	0.24	n.d.										
average	21.5	1.3	18.7	1.3	0.14											
4 Hr Rep A	29.7	0.8	27.2	1.6	0.10	n.d.										
4 Hr Rep B	31.9	1.4	28.7	1.6	0.16	n.d.										
average	30.8	1.1	28.0	1.6	0.13											
8 Hr Rep A	49.9	0.3	47.3	2.1	0.20	n.d.										
8 Hr Rep B	47.6	0.4	45.1	1.9	0.20	n.d.										
average	48.8	0.3	46.2	2.0	0.20											
12 Hr Rep A	66.9	0.1	64.1	2.4	0.25	n.d.										
12 Hr Rep B	58.6	0.2	55.9	2.1	0.40	n.d.										
average	62.8	0.1	60.0	2.3	0.47											
24 Hr Rep A	65.6	0.0	63.2	2.0	0.29	34.7	9.1	22.7	0.0	2.9	9.1	86.0	2.0	3.2	2.0	102.2
24 Hr Rep B	64.0	0.0	61.7	2.0	0.19	36.3	8.6	24.3	0.0	3.4	8.6	86.0	2.0	3.6	2.1	102.3
average	64.8	0.0	62.5	2.0	0.24	35.5	8.8	23.5	0.0	3.2	8.8	86.0	2.0	3.4	2.0	102.3

(n.d. = not done)

a Total in water phase is based on a total volume of 35 mL except for 48 hr samples which are based on the volume of supernatant (as the whole system was analyzed for the 48 hr samples). Calculations are given in Appendix E.

b 4-Chlorophenoxy-propionic Acid.

Table VII. **Accountability and Extractability of Radiocarbon from Soil Slurry Hydrolysis of 2,4-DP-p 2-EHE in Sandy Loam Soil Following Application at 3.0 ppm.**

		Water Phase						
Sample	DPM Applied	DPM/mL	mL in Supernatant	Total DPM in Supernatant	Total DPM Combined Soil Extracts[a]	Total DPM Soil Residual Solids	Total DPM Recovered	Percent Recovery[b]
0 Hr A	2,020,127	1,695	32.0	54,234		1,983,386	2,037,620	100.9
0 Hr B	2,020,127	1,858	32.0	59,460		2,016,716	2,076,176	102.8
4 Hr A	2,020,127	12,295	31.5	387,290		1,746,919	2,134,209	105.6
4 Hr B	2,020,127	13,354	32.0	427,328		1,746,074	2,173,402	107.6
8 Hr A	2,020,127	13,896	31.0	430,772		1,681,743	2,112,515	104.6
8 Hr B	2,020,127	16,650	32.0	532,812		1,648,280	2,181,092	108.0
12 Hr A	2,020,127	17,965	32.0	574,865		1,558,609	2,133,474	105.6
12 Hr B	2,020,127	20,950	32.0	670,409		1,507,657	2,178,065	107.8
24 Hr A	2,020,127	31,310	31.5	986,257		1,163,065	2,149,322	106.4
24 Hr A	2,020,127	32,258	31.0	999,983		1,128,019	2,128,022	105.3
48 Hr A	2,020,127	34,311	31.0	1,063,651	1,015,882	60,969	2,140,502	106.0
48 Hr A	2,020,127	34,117	31.0	1,057,633	1,002,733	64,619	2,124,985	105.2

a Only the 48 hour soil pellets were extracted.

b The percent recovery of applied radiocarbon had an overall mean ± S.D. of 105.5 ± 2.1 % for all samples.

Table IX. Distribution of Radiocarbon in the Water Phase and Soil Pellet Extracts from Soil Slurry Hydrolysis of 2,4-DP-p 2-EHE in Sandy Loam Soil.

Sample	PERCENT OF APPLIED DOSE															
	Total in Water Phase[a]	Product Distribution in Water Phase				Total in Soil Extract	Product Distribution in Soil Extract				Product Distribution in Total System					
		2,4-DP-p: Ester	2,4-DP-p: Acid	4-CPP Acid[b]	Un-knowns		2,4-DP-p: Ester	2,4-DP-p: Acid	4-CPP Acid[b]	Un-knowns	2,4-DP-p: Ester	2,4-DP-p: Acid	4-CPP Acid[b]	Un-knowns	Unextractable	Total
0 Hr Rep A	2.9	n.d.	n.d.	n.d.	n.d.	n.d.										
0 Hr Rep B	3.2	n.d.	n.d.	n.d.	n.d.	n.d.										
average	3.1															
4 Hr Rep A	21.3	0.2	19.8	1.3	0.00	n.d.										
4 Hr Rep B	23.1	0.3	21.1	1.7	0.00	n.d.										
average	22.2	0.2	20.5	1.5	0.00											
8 Hr Rep A	24.1	0.0	22.6	1.5	0.00	n.d.										
8 Hr Rep B	28.8	0.1	27.1	1.6	0.12	n.d.										
average	26.5	0.1	24.9	1.5	0.06											
12 Hr Rep A	31.1	0.1	29.4	1.6	0.00	n.d.										
12 Hr Rep B	36.3	0.0	34.4	1.8	0.08	n.d.										
average	33.7	0.1	31.9	1.7	0.04											
24 Hr Rep A	54.2	0.1	52.0	2.2	0.10	n.d.										
24 Hr Rep B	55.9	0.1	53.8	2.0	0.00	n.d.										
average	55.1	0.1	52.9	2.1	0.05											
48 Hr Rep A	52.7	0.0	51.0	1.7	0.00	50.3	30.3	17.3	0.3	2.3	30.3	68.3	2.0	2.3	3.0	106.0
48 Hr Rep B	52.4	0.0	50.6	1.8	0.00	49.6	30.2	17.4	0.0	2.0	30.2	68.0	1.8	2.0	3.2	105.2
average	52.5	0.0	50.8	1.8	0.00	50.0	30.2	17.4	0.2	2.2	30.2	68.2	1.9	2.2	3.1	105.6

(n.d. = not done)

a Total in water phase is based on a total volume of 35 mL except for 48 hr samples which are based on the volume of supernatant (as the whole system was analyzed for the 48 hr samples). Calculations are given in Appendix E.

b 4-Chlorophenoxy-propionic Acid.